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A Continuous Foaming Process of Low-Density PLA by Supercritical CO$_2$ Assisted Extrusion

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ABSTRACT

Polylactic acid (PLA) represents probably one the most viable environmentally-sustainable alternative to petrochemical-based plastics. This paper reports the continuous processing of PLA foams with CO$_2$ as the blowing agent. Different operating conditions were tested for a commercial linear PLA and the obtained foams were characterized on the basis of porosity and thermal properties. Finally, foams with expansion ratio up to 95% were obtained. The importance of the operating temperatures was emphasized, what requires the use of high CO$_2$ fractions. Higher crystalline contents than the raw material can be obtained, this content being linked to the process conditions and thus to the porosity.

INTRODUCTION

The Polylactic Acid (PLA) is a promising biobased and biodegradable thermoplastic material usually obtained by the fermentation of renewable resource as starch corn. Several applications have been proposed for this polymer in the fields of medicine, agriculture, and packaging [1, 2, 3, 4]. In order to further improve the toughness and widen the application of PLA, research works have continuously been made in PLA foaming technology, which is a well-known process to enhance the ductility and impact resistance by providing a significant expansion ratio and weight reduction [5, 6]. The high expansion ratio induced by foaming generally could reduce the material cost and consumption in mass-produced plastic parts without significantly impairing its other properties.

In this context, a great deal of attention has been given to supercritical carbon dioxide (scCO$_2$), due to its ability to solubilise in large quantities into many polymers. Recently, efforts have been made to produce PLA foams from scCO$_2$-assisted extrusion [7, 8, 9, 10, 11, 12]. The injection of scCO$_2$ into the barrel of an extruder modifies the rheological properties of the polymer melt and scCO$_2$ acts as a blowing agent upon depressurisation when flowing through the die [7].

Our laboratory has developed such an extrusion process [13, 14]. In the present work, it has been used to prepare PLA foams.

MATERIALS AND METHODS

Materials
PLA used in this study was purchased from Natureplast (PLE 001). According to the manufactures, it is semi-crystal-linear with a low D-lactide molar content.

ScCO$_2$ assisted extrusion

Hot-melt extrusion was performed using a single-screw Rheoscam extruder, which has a 30 mm-screw diameter and a length to diameter ratio (L/D) of 35 (Scamex, France) already described in details elsewhere [13] (Figure 1). The screw speed was kept constant at 20 rpm.

![Figure 1: experimental device.](image)

Four static mixer elements (Sulzer, SMB-H, 17/4), with a diameter of 17 mm and a whole L/D of 2, were added between the screw and the die to improve the mixing quality and thus minimising the plug flow effect [14].

The die used in these trials was a home made one, with an annular shape. It allowed controlling the backflow pressure inside the extruder by means of a pin controlled by an air counter-pressure.

Hopper temperature was fixed at 50°C. Barrel temperature was controlled separately in 5 zones: $T_1$ and $T_2$ before the CO$_2$ injection point, $T_3$ and $T_4$ after it, $T_5$ in the mixing zone and $T_6$ in the die. $T_1$ to $T_4$ were fixed for all experiments at respectively 160, 180, 180 and 160°C, while $T_5$ and $T_6$ were varied.

The state of the matter was controlled by five pressure sensors ($P_1$, $P_2$, $P_3$, $P_4$, and $P_5$) and three temperature sensors ($T_{mat1}$, $T_{mat2}$, and $T_{mat3}$) positioned along the path of the polymer.

Carbon dioxide was injected in the extruder barrel, at a L/D of 20 from the feed hopper at the same pressure as that of the extruder, using a syringe pump in a constant volumetric flow rate mode (260D, ISCO). CO$_2$ density obtained from the website of NIST [15] and calculated with
the Span and Wagner equation of state [16] was used to determine the CO$_2$ mass flow rate and the CO$_2$ mass percentage in the melt.

Once steady state conditions reached with the chosen operating conditions, extrudates were cooled at ambient conditions, collected and then characterised.

**Characterisation**

Thermal analyses were carried out by differential scanning calorimetry (DSC Q200, TA Instrument). Two cycles of heating-cooling from 20 to 200 °C have been applied with a heating rate of 5 °C/min. The crystalline content was determined during the first heating by the following formula [17]:

$$\chi = \frac{\Delta H_m - \Delta H_c}{\Delta H_f}$$

(1)

$\Delta H_m$ is the heat of melting, $\Delta H_c$ the heat of cold crystallisation and $\Delta H_f$ the theoretical heat of fusion of 100 % crystalline PLA. A value of 93.1 J/g was taken as PLA theoretical heat of fusion [17].

Porosity $\varepsilon$, defined as the ratio of void volume to the total volume of the sample, was calculated by Equation (1):

$$\varepsilon = 1 - \frac{\rho_{\text{app}}}{\rho_p}$$

(1)

$\rho_{\text{app}}$ is the apparent density calculated from the weight of the samples and their volumes evaluated by measuring their diameter and length with a vernier (Facom, France). $\rho_p$ is the solid polymer density, determined by helium pycnometry (Micromeretics, AccuPYC 1330), which is about 1270 kg.m$^{-3}$.

To complete the characterization of the porosity structure, samples were examined by scanning electron microscopy (ESEM, FEG, Philips).

**RESULTS**

The evolution of the porosity is shown on Figure 2. The porosity usually reaches a maximum when the melt strength balances the diffusion of the blowing agent, such that cells grow to their maximum without rupturing [18]. For a screw rotation speed equal to 20 rpm, the porosity increase as the temperature $T_6$ decreases, whatever the temperature $T_5$. No decay below a certain temperature can be observed, which is already known for most thermoplastics because of excessive melt strength [10, 18]. At a lower temperature $T_5$, higher porosity can be reached, with values up to 95 %, for a higher range of the die temperature $T_6$. As already observed, a compromise should be obtained between this two temperatures [7].

If the screw rotation speed is increased to 30 rpm (and thus the polymer mass flow rate) at a constant CO$_2$ mass fraction, a maximal porosity can be observed for $T_6=112$ °C at about 90 %, what is lower than the one at 20 rpm.
However, it has to be noted that the operating window for producing high porosity PLA foams is very narrow. Indeed, to reach the interesting range of temperatures, the polymer has to be plasticized with a sufficiently high quantity of CO₂ [17].

The morphology of the highly expanded foams can be observed on Figure 3. The structure is uniform with well-formed cells, which are rather closed one.

The results of the thermal analyses are presented in Table 1. As previously reminded, upon initial heating, the glass transition temperature $T_g$ and enthalpic relaxation peak of the PLA are followed by an exothermic cold crystallization (temperature $T_c$ and heat of crystallisation $\Delta H_c$) and by a well defined endothermic melting (temperature $T_m$ and heat of melting $\Delta H_m$).
For the raw PLA, $T_g$ is about 59 °C, the crystallisation temperature 101 °C and the melting temperature 152 °C. Based on the different enthalpies, the crystalline content is estimated to 0.5%.

For the two foams analysed, the characteristic temperatures remain more or less the same. However, the crystalline content $X_c$ is increased by foaming, the highest crystallinity corresponding to the highest porosity. Crystallinity seems to be determined by processing conditions and is known to be linked to the expansion ratio [8]. *In situ* formed crystal domains seems to supply nucleating sites to enhance cell nucleation and cell structure [12].

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g$ (°C)</th>
<th>$T_c$ (°C)</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_c$ (J/g)</th>
<th>$\Delta H_m$ (J/g)</th>
<th>$X_c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>raw</td>
<td>59</td>
<td>101</td>
<td>152</td>
<td>21.5</td>
<td>21.6</td>
<td>0.5</td>
</tr>
<tr>
<td>foam ($T_s$=145 °C)</td>
<td>57</td>
<td>102</td>
<td>155</td>
<td>22.3</td>
<td>27.0</td>
<td>5.0</td>
</tr>
<tr>
<td>foam ($T_s$=135 °C)</td>
<td>59</td>
<td>107</td>
<td>155</td>
<td>20.3</td>
<td>27.0</td>
<td>7.3</td>
</tr>
</tbody>
</table>

Table 1: thermal results of the raw PLA and two foamed samples ($T_s$=117±1 °C, $CO_2=7.3 \%$, $N=20$ rpm)

**CONCLUSION**

The extrusion foaming behaviour of a linear PLA was investigated using CO$_2$ as the physical blowing agent. Highly expanded foams with porosity up to 95% were obtained. Thermal analysis allowed to show that increased crystallinity can be obtained, this crystallinity being linked to the operating conditions. However, it has to be noted that low processing temperatures were necessary, what required high CO$_2$ mass fraction.

**REFERENCES**


